Metallization and Structural Transformation of Iodine under Pressure: A Microscopic View

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Elemental iodine has been studied by ^{129}I Mössbauer effect at 4 K to pressures of 30 GPa in a diamond anvil cell. Its structural transformations leading to metallization have been determined by the quadrupole interaction. At $P \gtrsim 16$ GPa an I_2—I_2 zig-zag chain is formed leading to its metallic behavior, and at $P \gtrsim 21$ GPa the formation of a quasi two-dimensional system is observed. Up to 30 GPa the I_2 molecule remains the building block of the high-pressure structural modifications.

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In recent years there has been an increased interest in the mechanisms of molecular dissociation and metallization under very high pressure in materials such as hydrogen and other diatomic molecular crystals.[1] Numerous experimental studies have been conducted making use of the newly developed very-high–static-pressure device, the diamond anvil cell[2] (DAC). Among those molecular crystals, elemental iodine has been the focus of several experimental and theoretical studies. It is the only elemental diatomic molecular crystal that has shown definite metallic behavior and experimental evidence for molecular dissociation at high pressure. At ambient pressure this molecular crystal has an optical energy gap of 1.35 eV, and with increasing pressure it becomes metallic at $\simeq 16$ GPa.[3,4] Drickamer and co-workers suggested that the onset of the metallic state could be reached either by the overlap of the conduction and valence bands as in a semimetal or by the formation of a monatomic crystal with an unfilled $5p$ conduction band. Extensive electrical measurements by Sakai *et al.*[5] to pressures of 25 GPa have confirmed previous conclusions[3,4] that for $P > 16$ GPa the slope of the resistance temperature dependence is positive and the thermoelectric power reaches values comparable to those of noble metals. Studies by x rays[6-9] failed to show any indication for a crystallographic phase transition in the vicinity of $P \simeq 16$ GPa that could be attributed to the onset of the metallic state. Raman spectroscopy on iodine to pressures of 21 GPa by Shimomura, Takemura, and Aoki[10] did not show decisively the extinction of the intramolecular vibronic lines, as expected for the case of a monatomic state. Because of the presence of conduction electrons in the high-pressure metallic state, the Raman lines broaden and the intensities decrease; this result inhibits this method as a useful probe for studying the evolution of new structures in iodine at higher pressures. This unsolved problem has motivated our present work, where for the first time iodine Mössbauer spectroscopy (MS) has been conducted at very high pressures.

Our high-pressure experiments were conducted in a Merrill-Bassett-type cell,[2] using diamonds with 0.8-mm-diam culets. The Mössbauer isotope was ^{129}I whose $\frac{5}{2} \rightarrow \frac{7}{2}$, 27.8-keV transition provides excellent spectroscopic features for studies of hyperfine interactions.[11] This fission-product isotope ($t_{1/2} = 1.59 \times 10^7$ yr) was purchased as a sodium iodide solution, from which PdI_2 was precipitated. Elemental iodine was obtained by thermal dissociation of the PdI_2. The sample chamber used was made of $Ta_{0.9}W_{0.1}$ alloy which served both as a gasket and as an effective collimator for the 27.8-keV γ ray. The chamber was formed by preindenting of the metal to 40 μm thickness and drilling a 210-μm hole in the center. The $^{129}I_2$ absorber with a thickness of 20 mg/cm^2 was loaded in an Ar atmosphere into the chamber together with ruby chips for *in situ* pressure calibration.[12] Pressures were changed at room temperature and were measured at several locations in the sample at room temperature and occasionally at 20 K. Pressure homogeneity was within 1–2 GPa. This absorber was used for both MS and Raman measurements. The ^{129m}Te source ($t_{1/2} = 33$ d) was obtained by irradiation of a 3-mm-diam pellet of Mg_3TeO_6 enriched with ^{128}Te in the Oak Ridge National Laboratory high-flux reactor for fourteen days.[13] Measurements were performed with source and absorber primarily at 4 K for more than fourteen pressures up to 30 GPa. Typical spectra, taken at 6, 21, and 27 GPa, are shown in Figs. 1(a), 1(b), and 1(c), respectively.

The spin Hamiltonian governing the quadrupole interaction in the ground ($I = \frac{7}{2}$) and excited ($I^* = \frac{5}{2}$) states can be written as follows:

$$H = \frac{e^2qQ}{4I(2I-1)}\left[3I_z^2 - I^2 + \tfrac{1}{2}\eta(I_+^2 + I_-^2)\right], \qquad (1)$$

where I_z^2, I_+^2, and I_-^2 are spin operators, eQ is the nuclear quadrupole moment, $eq = V_{zz}$ is the principal axis of the electric field gradient, and η is the asymmetry parameter; $\eta = (V_{xx} - V_{yy})/V_{zz}$ may vary between 0 and 1. The spectra were fitted by a computer least-squares-fit program based on the above Hamiltonian by the method of Shenoy and Dunlap[14] for polycrystalline materials. The free variables in the fitting procedure were the isomer shift, the linewidth, the total intensity, the quadrupole coupling constant (e^2qQ), and the η value. The

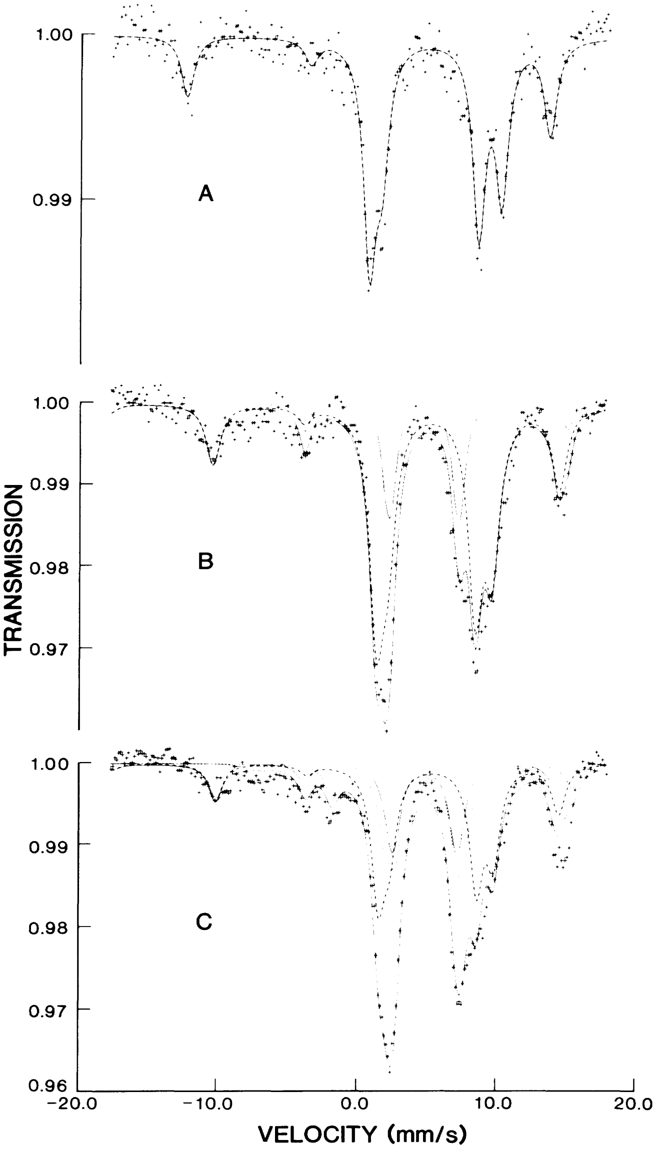

FIG. 1. ^{129}I Mössbauer spectra of elemental iodine in a diamond anvil cell measured at (a) 6 GPa, (b) 21 GPa, and (c) 27 GPa with a Mg_3TeO_6 source at 4 K. The lines through the experimental points are theoretical spectra obtained by a least-squares fitting procedure explained in the text. The lines of the spectral components are short-dashed line, long-dashed line, and dotted line for LP, HP1, and HP2, respectively. Each spectral fit is characterized by a single linewidth parameter that is independent of pressure or temperature; this is to be expected whenever the pressure gradients are small. The isomer shifts varied smoothly with pressure and temperature. Errors associated with η and e^2qQ are shown in Fig. 3.

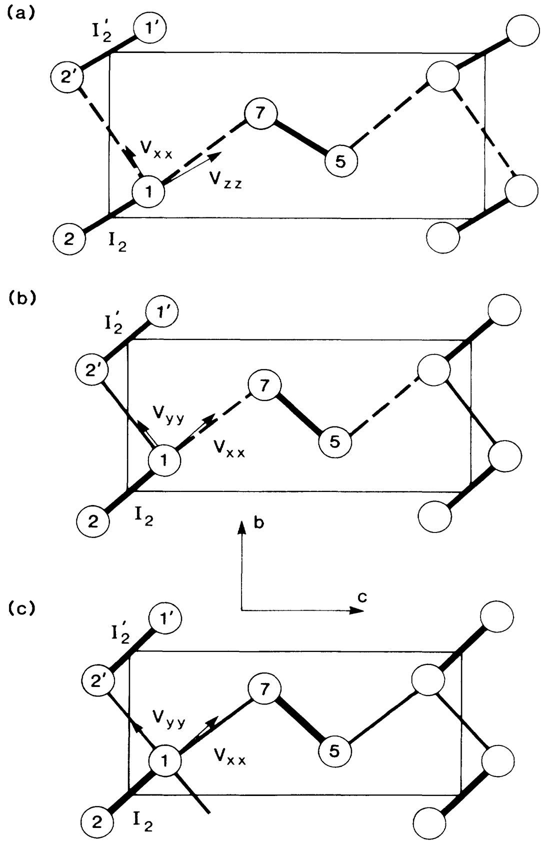

FIG. 2. Schematic representation of the proposed elementary steps in the high-pressure structural deformation of iodine. (a) The low-pressure, molecular phase. The principal axis of the electric field gradient, V_{zz}, is along the molecular axis, V_{xx} is in the b-c plane, and V_{yy} is perpendicular to the b-c plane. (b) The I_2—I_2 zigzag chain. This is a quasi one-dimensional structure suggested for HP1, that may be responsible for the metallic behavior of the conductivity in the pressure range $15 \leq P \leq 21$ GPa. V_{zz} is perpendicular to the b-c plane. (c) The two-dimensional HP2 structure.

spectrum in Fig. 1(a) is typical of the low-pressure (LP) range ($0 \leq P \leq 16$ GPa) where one distinct spectral component is observed characterized by a *negative* e^2qQ.

From both nuclear quadrupole resonance[15] and MS[16] studies, it is well established that V_{zz} lies along the molecular axis of I_2 [see Fig. 2(a)] and its positive sign (eQ is negative) is due to the p_z-hole deficiency in the closed $5s^25p^6$ configuration.[15] It is noteworthy that V_{zz} even at ambient pressure is not axially symmetric as would be expected for pure van der Waals forces in a molecular crystal. The finite value of $\eta = 0.18$ at $P = 1$ bar is consistent with a finite molecular overlap in the b-c plane of the I_2 crystal. With increasing pressure (see Fig. 3), η increases and $|e^2qQ|$ decreases; this can be explained as due to the delocalization or removal of p holes from the intramolecular into the intermolecular orbitals. In the vicinity of 16 GPa a new spectral component appears, designated as HP1, characterized by a *positive* e^2qQ with an absolute value considerably lower than that of the LP component and by $\eta \simeq 0.8$. The flip in sign of V_{zz} indicates the onset of an I_2—I_2 long-range

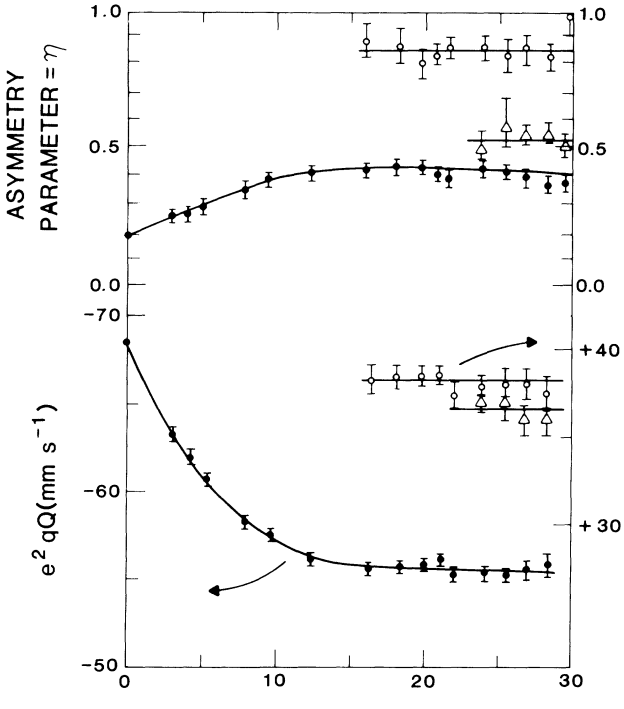

FIG. 3. The pressure variation of the quadrupole coupling constant e^2qQ and the asymmetry parameter η. Note the change from LP in sign and absolute value of e^2qQ for both the HP1 and HP2 components. Filled circles, triangles, and open circles correspond to LP, HP1, and HP2, respectively.

species as illustrated in Fig. 2(b). The significantly large value of η reflects the strong intramolecular bonding ($V_{xx} \gg V_{yy}$) still prevailing in this phase. The pressure at which this new component appears coincides with that where the metallic state is formed, namely the pressure where the optical gap disappears and the onset of the conduction- and valence-band overlap[1,2,5] appears. It is noteworthy that from x-ray pressure data[9] the intermolecular distance $r_{12'}$ exceeds the r_{17} distance at low pressures [see Fig. 3(a)], equals r_{17} at around 14 GPa, and becomes shorter with further increasing pressure. It seems that this crossover in intermolecular distances at the b-c plane may be crucial to the onset of the metallic state and to the enhancement of the $|\psi(I_2')_{p_y}\psi(I_2)_{p_y}|^2$ intermolecular overlap. With increased pressure more of the HP1 species is formed, as measured by the relative intensities of the MS spectra, and the strength of the overlap increases as expected from the shrinkage of the $r_{12'}$ distances.[9] This suggested model of a zigzag chain [see Fig. 2(b)] of overlapping I_2 molecules and a relatively weak interchain interaction—a quasi one-dimensional system—may explain the absence of new x-ray diffraction lines in the 15–21-GPa range as well as the unusual temperature dependence of the resistivity at 17 GPa.[5]

With increasing pressure, at $P \simeq 24$ GPa, a third MS spectral component appears, designated as HP2. It is characterized by the same hyperfine interaction constants as HP1 but with a considerably lower value for η (see Fig. 3). The decrease in the η value is due to the enhanced interaction between the nearest-neighbor chains to form ultimately a quasi two-dimensional conductor in the b-c plane [see Fig. 2(c)]. Careful resistivity measurements by Sakai *et al.*[5] in this region have shown a small peak ($\simeq 2\%$) at $P = 22.5$ GPa, and low-temperature resistance measurements at $P = 23.5$ GPa clearly display a resistivity power-law behavior, which is based on the Grüneisen-Bloch equation. The value found for the temperature exponent was 3.7 which is considerably lower than 5, the value expected for a three-dimensional monovalent metal.[17] The power-law behavior and the value of 3.7 suggests a metallic conductivity of a two-dimensional system[18] and supports our spectroscopic observations.

We note that a new x-ray diffraction pattern at $P \simeq 21$ GPa was observed by Takemura *et al.*[8,9] This has been interpreted as a first-order phase transition into a *monatomic* body-centered orthorhombic lattice (D_{2h}^{25}-I_{mmm}). The assignment of this new crystallographic phase to a monatomic structure is, in our opinion, inconsistent with our results as well as with the electrical conductivity measurements for the following reasons: (1) A first-order transition into a monatomic iodine phase would result in the formation of an unfilled p-hole conduction band producing a significant change of the resistivity at $P \simeq 21$ GPa. Despite careful measurements[6] such a change has not been observed. (2) The x-ray analysis[9] of the HP2 phase provided the following lattice constants: The interplanar distance $b_H = 5.252(9)$, and the intraplane distances of $c_H = 2.904(9)$ and $a_H = 3.031(4)$. The constant c_H corresponds to the LP intramolecular distance r_{12} whereas a_H corresponds to the intermolecular distances r_{12} and r_{17}. The deviation from a b-c tetragonal structure is barely 4%. The 90° angle formed by the iodine atoms and their almost identical spacings in the plane, as suggested by this analysis, cannot explain the high asymmetry parameter η found by MS. In other words, such a structure would have resulted in quasi fourfold symmetry ($V_{xx} \simeq V_{yy}$) at the plane with an axially symmetric V_{zz} ($\eta \simeq 0$).

In summary, molecular dissociation of iodine has not been observed in our ^{129}I MS. A new structural phase, HP1, is observed at $\simeq 16$ GPa. This structure is probably of low dimensionality, coexists with the molecular phase, and is responsible for the onset of the metallic behavior of the conductivity. At $P \simeq 24$ GPa a second high-pressure phase, HP2, with a two-dimensional structure, is observed that is characterized by an enhanced interchain interaction in the b-c plane; this conclusion is based on the decrease in η and negligible change in e^2qQ with respect to HP1. HP2 is likely related to the small peak in the resistivity and to the presence of a new phase detected by x-ray diffraction. Our results point to a diatomic character of iodine in both HP1 and HP2 structures. Raman studies of our sample to $P=30$ GPa show a distinct broad line at the vicinity of 210 cm^{-1}, characteristic of a persistence of the I_2 intramolecular stretching mode.[10] The evolution of the new structures with increased pressure is gradual, reaching in our sample a total abundance of 62% for HP1+HP2 at $P=30$ GPa.

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